Ab initio Simulation Study on the Control of Electron Transport in Molecular Device (分子デバイス中の電子伝導制御に関する第一原理シミュレーション研究)

	りー さん うく
氏　　名	李　常　旭
授与学位	博士（工学）
学位授与年月日	平成２０年９月１１日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）知能デバイス材料工学専攻
学位論文題目	*Ab initio* Simulation Study on the Control of Electron Transport in Molecular Device（分子デバイス中の電子伝導制御に関する第一原理シミュレーション研究）
指導教員	東北大学教授　川添　良幸
論文審査委員	主査　東北大学教授　川添　良幸　東北大学教授　阿尻　雅文 東北大学教授　鈴木　誠

論文内容要旨

This thesis presents the controlling factors of the electron transport in the molecular junctions through the understanding of the electronic and transport processes at the single molecular level. In order to have a thorough understanding, we develop a computationally efficient approach to do an analysis of single-molecule at the open system based on the density functional theory (DFT) and non-equilibrium Green's Function (NEGF) formalism. We use this approach to treat several molecular junctions constructed by metal electrodes and several nanostructures, such as small organic molecules, bio-molecules, carbon nanotubes (CNTs), and nanowires.

The drive toward further miniaturization of silicon-based electronics has led to a renewal of efforts to build devices with molecular-scale components. The miniaturization of components is currently pursued by a "top-down" approach. However, it is becoming clear that t e top-down approach is subject to drastic limitations of fabrication and the law of quantum mechanic To proceed toward nano-scale, science and technology need to find new avenues. A promising strate to exploit science and technology is the "bottom-up" approach.

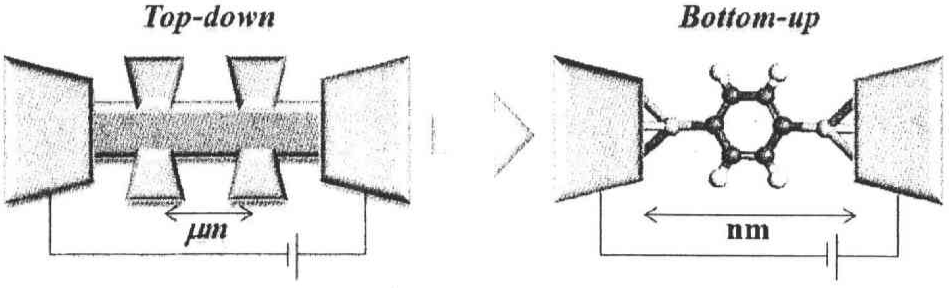


Figure 1 Schematics of conventional microelectronic device and molecular electronic device.

In this regard, "Molecular electronics" has emerged as a next-generation technology because of the fact that useful devices can be built on the basis of individual molecules. Since the advent of molecular electronics, an abundance of organic functional molecules have been designed and investigated as components in electronic devices such as molecular wires, rectifiers, and switches. Accompanied with the synthesis of functional organic molecules, the advancement of techniques for characterizing and manipulating individual molecules and the availability of first-principles methods to describe electron tunneling through atomic chains or single molecules, make it possible to realize molecular electronic devices.

Molecular electronics will mature into a powerful technology only if its development is based on sound scientific conclusions that have been tried and tested at every step. Reaching these objects requires a detailed understanding of the electronic and transport processes at the single molecular level, as well as developing methods for manufacturing reliable devices and ensuring their robustness. In this work, a series of theoretical analyses were devoted to the designed molecular devices with single molecule or molecular strands in order to have the basic physics in the molecular electronic devices and to determine the factors controlling the electron transport.

An introductory discussion of the NEGF formalism and details of the developed program code can be found in **Chapter 2.** The code calculates the current-voltage (I–V) characteristics and conductance spectrum (G-V) of a molecule sandwiched between two metallic contacts. Equilibrium properties such as density of sates (DOS) and transmission function can also be computed. These calculations are performed using "Density functional theory" (DFT) and "Non-equilibrium Green's function formalism" (NEGF). This code is implanted to Gaussian03 package.

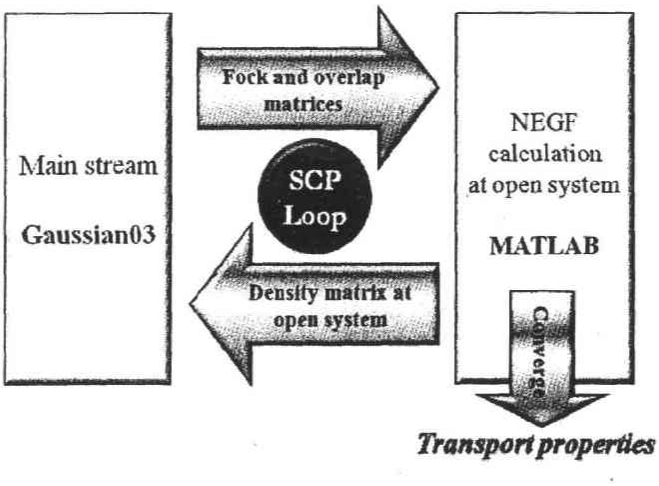
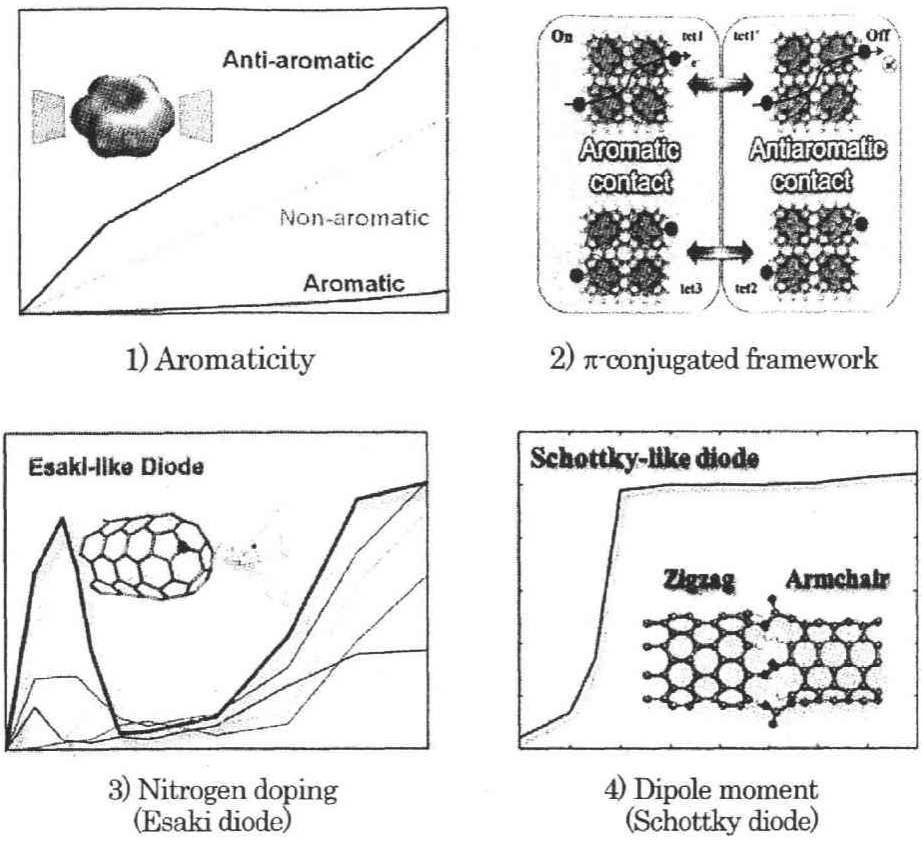


Figure 2 Scheme of developed program code based on NEGF.



1) Aromaticity

2) π-conjugated framework

3) Nitrogen doping (Esaki diode)

4) Dipole moment (Schottky diode)

Figure 3 Controlling factors of electron transport at the molecular device.

Our simple strategies to control the electron transport are based on 1) aromaticity, 2) π-conjugated framework, 3) doping, and 4) dipole moment. Each topic is demonstrated from Chapter 3 to Chapter 6.

In **Chapter 3**, we will consider the aromaticity as a factor controlling of electron transport. We present three types of models based on the para terphenyl (PTP) molecule composed of three phenyl rings, where the central phenyl ring is replaced to the anti-aromatic or non-aromatic components. Considering a delocalized orbital network in the conjugated system, both aromatic and anti-aromatic molecules contain an uninterrupted □ electron cloud allowing the electrons to flow easily around the molecule despite of different chemical and physical properties of the molecules. Therefore, it is of interest to compare the electron transport characteristics of conjugated molecules containing the distinct conjugated framework.

In **Chapter 4**, we will consider the π–conjugated framework as a factor controlling of electron transport. We present that the electron transport characteristics can be controlled by manipulating the π–conjugated framework in the multiporphyrinic systems through the arrangement of the inner hydrogen atoms. The designed π–conjugated framework assigns the distinct aromaticity on the contact structure, and the large aromatic nature of the contact structure increases conductivity.

In **Chapter 5**, we will consider the doping, especially nitrogen atom, as a factor controlling of electron transport. We present that the tunneling current between two N-doped capped CNTs is dramatically increased by nitrogen doping and the current-voltage curve shows negative differential resistance (NDR), which is a characteristic feature of the Esaki-like diode, i.e. tunneling diode. The NDR behavior can be understood by a rigid shift model of the HOMO- and LUMO-filtered energy levels under the applied biases.

In **Chapter 6**, we will consider the dipole moment as a factor controlling of electron transport. We design a rectifying diode by carbon nanotube intramolecular heterojunction with peptide linkage. We present that the incorporation of peptide linkages and their associated dipole moments play an important role in determining their electron transport characteristics and lead to materials with unique properties, such as Schottky-like behavior.

"Molecular electronics" pose a distinct set of challenges, both in the understanding of the electron transport at the single molecular level and the embodiment of device with interesting device characteristics. In **Chapter 7**, we show that the designed junctions with single-molecule and low-dimensional carbon allotropes (namely fullerene, CNT, and recently graphene) open the door to the design of nanogadgetry embodied with interesting device characteristics, namely "Computer-Aided Nanodesign". When we inserted Zn metal layers within metallic CNT electrodes thereby providing 1D heterojunctions that can act as a wire-like, NDR, or varistor-type nanoscale device. In general, the preceded theoretical investigations allow experimental researchers to avoid starting costly experiments by choosing preferentially the way which has no serious objections from a theoretical point of view. Therefore, we strongly believe that our results will give an insight into the design and implementation of various electronic logic functions for applications in the field of nanoelectronics.

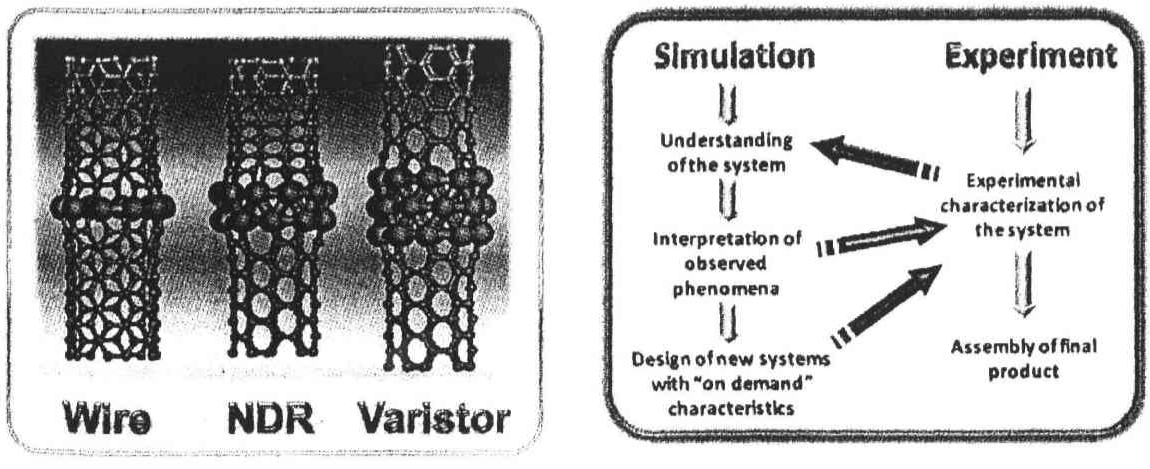


Figure 4 Computer-Aided Nanodesign.

論文審査結果の要旨

本論文は、シリコンテクノロジーの終焉後の新集積回路技術として期待される分子エレクトロニクスに関して、非平衡グリーン関数理論による計算手法及びそれを活用したスーパーコンピューターによる超大規模シミュレーション計算による新ナノ物質予言法を確立し、具体的な応用例を実用レベルを想定して提示したもので、全編８章よりなる。

第１章は序論であり、分子エレクトロニクスの概要とシミュレーション計算による従来の実験と理論に次ぐ新しい研究手法を述べている。

第２章では、非平衡グリーン関数法の分子エレクトロニクス研究への適用方法をまとめ、本研究のために今回独自に開発した第一原理計算手法を述べ、具体的な計算機システムへの実装方法について詳述している。

第３章では、分子エレクトロニクス材料中の電子伝導特性を制御する方策として、共役系の操作を取り上げ、具体的な分子を対象とした第一原理シミュレーション計算を実行した。NiPTP や CoPTP4 等が特に良好な電子伝導特性を有することを確認することに成功した。

第４章では、単分子スイッチの例として、複合ポルフィリン系を取り上げ、その電子伝導特性の詳細を第一原理シミュレーション計算によって検討した。当該分子中の電子伝導を数値的に精密に追跡し、芳香族性が電子伝導特性を制御する主たる要因である事を明らかにした。

第５章では、窒素をドープしたカーボンナノチューブを対象として、その電子伝導特性の詳細を理論的に解析し、ナノ電子デバイスのデザイン方策を確立した。ナノスケールのデバイス要素に対する数値的解析による実験以前の予言方策を与える事に成功した事例である。

第６章では、ペプチド環によって結合された異なるカイラリティを有するカーボンナノチューブ中の電子伝導特性を第一原理シミュレーション計算によって予測した。

第７章は、亜鉛環をはさんだカーボンナノチューブ中の電子伝導特性を取り扱っている。亜鉛層の調整により、ワイヤー、バリスター、ダイオード等の分子エレクトロニクス要素として有効な特性を持たせることが可能であることをはじめて明らかにすることが出来た。

第８章は総括である。

以上要するに、本論文は、新ナノ材料を活用し、将来の集積回路中の電子伝導特性を予測し、最適な回路設計に応用する為の研究基盤を確立したもので、材料物性学の発展に寄与するところが少なくない。よって，本論文は博士(工学)の学位論文として合格と認める。